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COATING OF PLASMA POLYMERIZED FILM

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16. Abstract The process of plasma polymerized film coating is discussed from the viewpoint of polymerization conditions in the reaction.			
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COATING OF PLASMA POLYMERIZED FILM

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I. Introduction

Demands for new techniques are being met by the distinctive characteristics of plasma polymerized film and the method of coating.

For example, the method of coating, by plasma polymerizing, the resist film used in electron beam lithography has been changed from wet application to dry application under pressure.

Moreover, if we could develop a diagram of the electron beam by using plasma etching, the main process of the LSI formation would be done with the dry formula. It would become possible to complete the LSI within one of the vacuums [1,2].

The significance of the dry process is not well known and we have noted that it is possible to fundamentally change the process system of LSI formation.

In Figure 1 the methyl methacrylic acid film of plasma polymerization coats a chrome evaporation glass substrate. A line that is 10 μm wide is drawn by the electron beam and developed by carbon tetrachloride plasma etchings. We have shown that the line, which is transcribed on top of the chrome film plate, is observed in SEM [1,2].

The target pellet, which drives the energy of the nuclear fusion laser [4], is a globular fuel with a diameter of between 50 μm [5,6]. This globular fuel has many layers of film. Plasma polymerization has been tested as a coating method for glass, film with a small atomic number on top of metal pellets or powder layers. In the selection of

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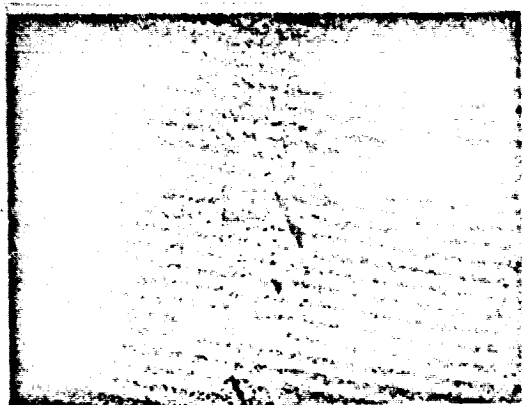


Figure 1.

pellet coating, there are many problems [7]. For example, how can we coat a high molecular film evenly on a spherical surface? The methods of plasma polymerization are being seriously considered [8,9].

Other than those items explained above, plasma polymerized thin film coating and the use of other coatings is suggested for passivation film,

thin film used for conducting light and solid body lubrication film of dielectrics of ultra-insulators for electrical conduction, electron accessories, etc. Many authors have previously presented ideas concerning the reaction of organic gases which develops in the glow discharge and an example of the application of plasma polymerized film [10-16]. We refer to these authors in this article. Therefore, in this manuscript we will show the special features of glow discharge development and the polymerized film growth mechanism.

2. Glow Discharge in an Organic Gas

We have observed plasma polymerization reactions even in inorganic compound gases, such as carbon monoxide, nitrogen and hydrogen [17]. However, in general, the reactions are found in organic gases. Thus, here we will limit our explanation to plasma polymerization in organic gases.

In plasma polymerization, the inorganic gas temperature is low and the temperature of the electrons is high in order not to pyrolyze that gas. We use what is called plasma at inequilibrium. This discharge, which can realize unequal plasma, generally is called glow discharge. When the gas pressure is 1 mm Hg, the parallel electrodes are established and separated by a number of cm. When 50 Hz or 60 Hz alternating current voltages are passed between the electrodes, a discharge is produced of about 1000V. A stable discharge continues at a discharge

current of several mA/cm^2 .

In Figure 2, three radiation spheres are observed. These are turned on and off with each alternation of the alternating current voltage. We can see the radiation continue with our own eyes. Each radiation sphere is a negative glow and there is a solar column between each of the electrodes. These physical characteristics of the radiation

sphere are thought to be very similar to the case of direct current glow discharge [18-20].

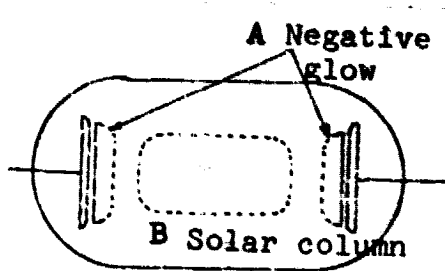


Figure 2

The discharge frequency is increased when the inertia of the ions and electrons becomes apparent. At the same time, the discharge continues with the supply of electrons from the

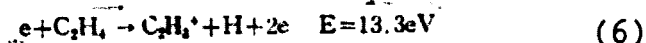
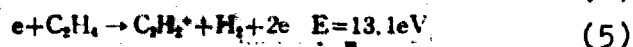
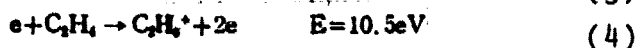
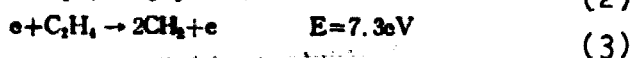
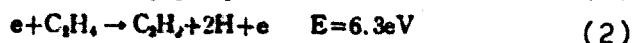
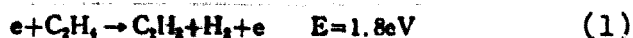
cathode. Only the discharge of the solar column, without a negative glow, is observed. Therefore, even in this case, the supply of the electric charge must exceed the size of the discharge current and a negative glow is formed [21].

Plasma at inequilibrium is changed to plasma at equilibrium when the gas pressure, electrical discharge power and discharge frequency are increased. The discharge of 1 atmospheric pressure is equilibrium plasma and when we add a voltage pulse of several μ seconds, the inequilibrium plasma can be realized [22,23].

There is also equilibrium plasma in the case of a discharge from microfrequency. When the gas pressure is very low, the plasma becomes unequal [22].

Ionization and excitation of organic gas in a glow discharge occurs in cases where the anode and the full spectrum column are somewhat different. Inactive gases, such as helium and argon, differ from organic gases because the gas molecules are decomposed. Investigation of the existence of this decomposed gas is essential.

For example, in the case of ethylene, we can first consider the following reactions [25].



In contrast to the ionized energy of ethyl, which is 10.5 eV, the decomposed energy is small, less than 7.3 eV. Consequently, many acetylenes are formed. Usually when acetylene is polymerized, the hydrogen atom is also activated and contributes to the polymerization reaction.

In halogen compounds, nitrogen compounds and oxides, the distinguishing characteristics affect the peculiarity of the polymerization reaction and the polymerized film by the variety of atoms that are included. For example, in contrast to the fact that nitrogen is easily taken into polymerized film, oxygen is difficult to introduce into the film [26]. When halogen is mixed with hydrocarbons, the rate of polymerization increases [27].

The gas molecules inside the glow discharge are also excited by external electron acceleration. These are radiation of light, free radicals or excited molecules and atoms. The other molecules are ionized and discharged by semistable, excited atoms. This development is known as the panning effect [18,20,28-30].

There is a large influence exerted on discharge and polymerization by this type of discharge.

The ionization voltage of the representative gases are shown in Table 1 [31]. The ionization voltage is an important physical quantity in knowing the set conditions of chemical reactions. However, the many cases of immediate opposition to polymerization reactions are difficult [32]. First, each type of energy excitation, energy decomposition and collision capacity of the gas molecules are compositely gathered and each reaction process must be considered.

Table 1. The Ionization Voltage
of Each Gas Molecule [31]

Gas molecule	Ionization voltage
Ar	15.8
H ₂	15.4
O ₂	12.1
H ₂ O	12.8
CH ₄	13.0
C ₂ H ₂	11.4
C ₂ H ₄	10.5
C ₂ H ₆	11.7
C ₃ H ₈	9.1
C ₄ H ₈ -CH=CH ₂	8.9
CH ₃ Cl	11.5
CH ₃ I	9.7

Today we cannot say that we have sufficient measurements of these physical properties.

3. The Process of Forming Plasma Polymerized Film

When we think of the formation of plasma polymerized film, we must consider the contribution of ions, electrons, free radicals, active particles and light radiation. All of these particles are found in the electric discharge as energy particles.

In general, the gas pressure, the quantity of gas flow, the electrical discharge power (or discharge current), and the discharge frequency are the parameters which regulate the reaction of plasma polymerization.

The formation of the discharge container and electrode system, the discharge form, the discharge frequency form, the gas temperature, and substrate temperature also exert an influence on the polymerization reaction and on the characteristics of the polymerized film.

Many parameters are essential to the plasma polymerization reaction when considering changes in electric discharge, such as the restraint of the plasma polymerization reaction and the size of the reaction chamber.

The formation process of plasma polymerized film can be considered by dividing the polymerization process into the excitation of gas molecules and the transport of excited molecules. Generally, excitation is carried out at the solid phase [33]. These reactions end after a short period of time. Therefore, the rate of plasma polymerization is determined from the transport process. The transport process differs considerably, depending upon the electrically charged particles and the neutral particles. The electrically charged particles are affected by the electrical discharge field and the distribution of electrical charges in the air. The neutral particles depend to a large extent on the diffusion of gas flow.

When plasma polymerized film is formed by the reaction of high energy particles that collide with the molecules adhering to the top of the substrate, the rate of formation of the polymerized film is expressed by the following formula.

$$W = \frac{M}{L\rho} P \quad (7)$$

Here M is the mass of the molecule, L is Loschmidt's number, ρ is the density of the polymerized film and P is the unit of time. Thus, the formula is the number of polymerized molecules per unit of area. When we find the molecular number, which coincides with the substrate, ϕ , the coefficient of the adherence γ , and the high energy number which coincides with the substrate R , we have the molecular number of the molecule gn that collides with substrate per 1 molecule of high energy, as shown in (8) [34].

$$P = \frac{\gamma\phi}{1 + \gamma gn R} \quad (8)$$

When the electrical discharge power or electrical discharge current is small, it becomes $\gamma\phi > gn R$ and

$$P \approx \gamma\phi \quad (9).$$

When the electrical discharge power or the discharge current is sufficiently large, we have $\gamma\phi < gn R$ and

$$P \approx \frac{\gamma\phi}{gn R} \quad (10).$$

The rate of formation of the polymerization film does not depend upon

electrical discharge power.

The method of contribution related to the plasma polymerization of these three components strongly depends upon the electrical discharge parameter and the discharge frequency, in particular. In the direct current discharge, the rate of formation of polymerized film is determined mainly by the drift component of the electrical field. When frequency increases, its contribution increases in proportion to the frequency of the ions from the electrical charge in the air. Moreover, in a high frequency field the components from the electrical charge of the ions in the air are decreased by the inertia of acceleration of the ions and electrons and only the components caused by the diffusion of both polarities. One example is shown in Figure 3.

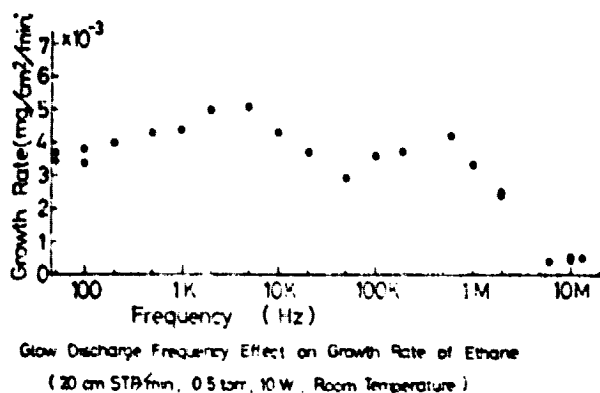


Figure 3.

As with the free radicals and activated particles, the electrically neutral, high energy particles also participate in plasma polymerization [38]. In the glow discharge we can also say that the density of the radical is higher than the density of the electrically charge particle by more than 1 [term unknown] [39]. The neutral particles are conducted only by diffusion. Therefore, generally,

the transport rate is low and the contribution to the plasma polymerization film rate is small. However, when the charged particles have a considerable degree of inertia in a high frequency range, the components caused by the diffusion of neutral particles cannot be ignored.

As shown in Figure 4, in a low frequency electrical discharge range, the plasma polymerization rate influences the gas flow [38]. This affects the decomposition of gas molecules in the electrical discharge and the free radicals.

4. Plasma Polymerized Film Coating

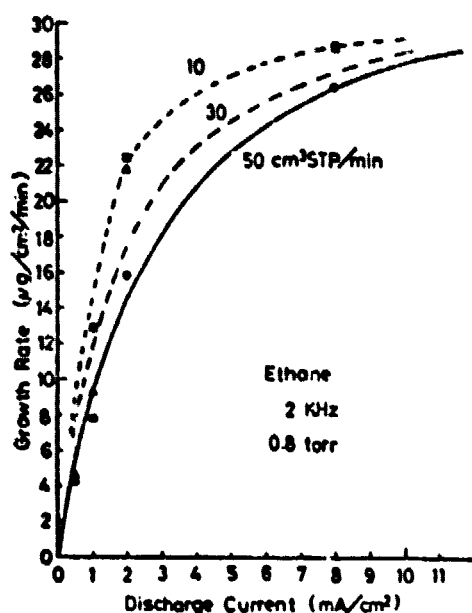


Figure 4.

In coatings of thin films that are plasma polymers, it is best if we choose conditions where the polymerization is performed on solid bodies. However, when we choose to carry out the reaction on gases, powder polymers are formed. In this way, the form of the plasma polymerized film and the properties of the film depend upon the polymerization conditions [39-41].

As in resistive film coatings, the molecular composition of polymerization films (in the case where a strong influence is exerted, as in resistive films), the selection of the polymerization method of monomers and the type of monomer are important

considerations.

In pellet coating, when the film condition and uniform membrane thickness in the coating are more important than the molecular structure, the treatment of the pellet, the adjustment of the flotation equation and the restraint of the electrical discharge are important.

In the application of plasma polymerized film to electron and light conductors, the treatment of the remaining, free radicals in the polymerized film involves the peculiarities of the polymerized film and the life span. Therefore, all of these are important considerations.

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